Proposal for Direct Observation of Reorganiza-tion Energies Associated with Redox Change of an Active Center in Large Adsorbates, such as ET Proteins, by the V-I Characteristics of Photo-Induced STM Currents

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Scanning tunneling microscopy (STM) is very powerful in providing an atomic-scale image of conducting materials. It has also been pursued to obtain an atomic-scale image of large biomolecules, such as DNA and proteins, putting them as adsorbates on the substrate of STM, although they themselves are not conducting. Apart from such a direction of investigations, the V-I characteristics of the STM current carries a fruitful information about electronic properties of adsorbates. In this context, electron-transfer (ET) proteins are interesting and important. In this case, the STM current is mediated by a redox active center which is immersed as a prosthetic group in the protein matrix in order to enable biological ET processes by the proteins.

The rate constant of such ET's is determined essentially by three factors, the free energy of the ET reaction ΔG, the electronic matrix element J between the donor and the acceptor for ET, and the reorganization energy λ associated with the redox change of the active center. ΔG can be directly derived from the equilibrium constant for the reaction. J can be obtained from electronic-state calculations. Such calculations, however,have not been developed enough yet to give reliable values of λ, since it is determined by how large reorganization of the protein matrix occurs in association with the redox change of the active center. Therefore, it is very convenient if we have a method to experimentally derive λ for each ET protein. The total reorganization energy associated with ET between two ET proteins is given by the sum of λ's for them.

It was pointed out independently by the present author [1] and Kuznetsov, Ulstrup and collaborators [2] that the reorganization energy λ for each ET protein can be derived from the line-shape analysis of the V-I characteristics of the STM current between metallic electrodes. Let us set the redox center in the protein at height α from the substrate relative to the tip with $0 < \alpha < 1$, and also the reduction potential energy of the redox center at G_m (> 0), without bias, relative to the Fermi energy common for both the tip and the substrate. As a typical case, we set G_m as larger than λ which is usually of the order of 0.1 eV. In this case, at low temperatures the STM current rises almost steplike at both a positive bias energy of $\phi_c \equiv (G_m+\lambda)/(1-\alpha)$ and a negative bias energy of $\phi_d \equiv -(G_m+\lambda)/\alpha$ [1] Accordingly, the differential conductance constitutes a sharp peak at these bias energies, and the peak corresponds to the Marcus parabola [3] obtained electrochemically. Since the width of the Marcus parabola is λ multiplied by an additional temperature-dependent factor, we can derive λ in principle from the line-shape analysis of the peak. In this case, however, λ cannot be obtained directly as a voltage difference.

In many cases, the redox center in the protein can accept also optical excitation to its excited state. Because of a hole in the highest occupied state of the redox center, the excited state has a reduction potential energy lower than the ground state. The difference agrees with the energy difference Δ of the two states, which is usually 1 to 2 eV. As long as the bias energy is not very high [to be more exact, not higher than $(G_m+\Delta+\lambda)/(1-\alpha)$ or not lower than $-(G_m+\Delta+\lambda)/\alpha$)], the redox center with the excited state is rapidly reduced by ET from an electrode. Therefore, the photoexcitation of the redox center results in its reduction, and induces the STM current, which we call the photo-STM current. We can show that the current rises almost steplike at both a positive bias energy of $\phi_{c'} \equiv (G_m-\lambda)/(1-\alpha)$ and a negative bias energy of $\phi_{d'} \equiv -(G_m-\lambda)/\alpha$ [4]. Both $\phi_{c'}$ and $\phi_{d'}$ are located between ϕ_c and ϕ_d where the usual STM current is strongly suppressed at low temperatures [1]. Therefore, the steplike rises of the photo-STM current will easily be detected although its magnitude will be .1 to .01 times as small as that of the usual STM current, dependent also on the light intensity.

Since $\phi_c - \phi_{c'} = 2\lambda/(1-\alpha)$ and $\phi_{d'} - \phi_d = 2\lambda/\alpha$, we can derive λ and also α directly from the electrochemical voltage-difference measurement of $\phi_c - \phi_{c'}$ and $\phi_{d'} - \phi_d$ for each ET protein.

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